The Thermal [2+2] Cycloaddition of 1-Halo-2-(9-fluorenylidene)ethylene to Afford Fluorene-9-spiro-1'-[2'-halo-3'-(9-fluorenylidene)-4'-halomethylene]cyclobutane

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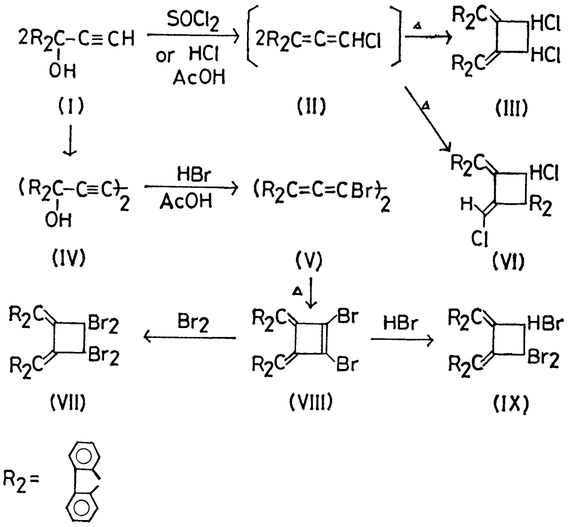
The thermal [2+2]cycloaddition products of 1-chloro-(II) and 1-bromo-2-(9-fluorenylidene)ethylene (X) were found to be two head-to-tail dimers, fluorene-9-spiro-1'-[2'-chloro-3'-(9-fluorenylidene)-4'-chloromethylene]-cyclobutane (VI) and its bromo-analog (XI) respectively.

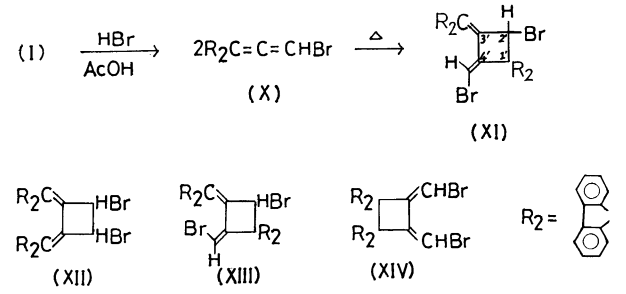
It has previously been reported[1] that the previously-assigned structure[2] 1-chloro-2-(9-fluorenylidene)ethylene (II) for the compound which was produced by the reaction of 9-ethynyl-9-hydroxyfluorene (I) with $SOCl_2$, is erroneous; rather, it is the head-to-head [2+2] cycloaddition dimer of II, 3,4-dichloro-1,2-bis(9-fluorenylidene)cyclobutane (III) (Scheme 1). We have now studied on the structures of the dimers of II and its Br-analog (X), and found that these dimers are two head-to-tail cycloaddition products, fluorene-9-spiro-1'-[2'-chloro-3'-(9-fluorenylidene)-4'-chloromethylene]cyclobutane (VI) and its Br-analog (XI) respectively.



Scheme 1.

On the reaction of I with concd HCl in AcOH at 0 °C, II could not be isolated, but its head-to-tail cycloaddition dimer (VI) was obtained. The UV spectral data of VI were identical with those recorded for the dimer of II.[1] The heating of the Br-analog of II (X), which could be isolated by the reaction of I with concd HBr in AcOH, afforded the head-to-tail cycloaddition dimer (XI). The spectral data of XI were comparable to those of VI.

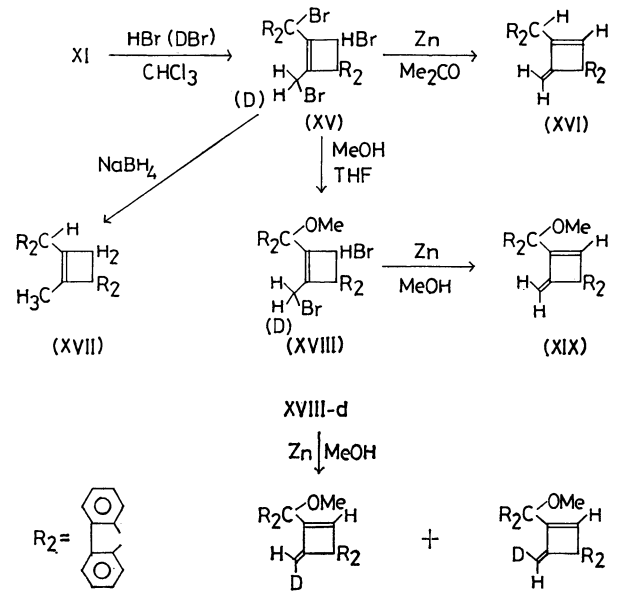
It is clear that the dimers of II and X were not the heat-to-head dimers, III and XII respectively, because the UV spectra of VI (276 (ε, 54000) and 375 nm (30000)) and XI (274 (ε, 51400) and 380 nm (32800)) differ widely from those of 3,3,4,4-tetrabromo- (VII) (278 (ε, 38600), 338 (9000) and 502 nm (23900)) and 3,3,4-tribromo-1,2-bis(9-fluorenylidene)cyclobutane (IX) (270 (ε, 30500), 328 (12700) and 472 nm (21400)), which were prepared by the addition of Br_2 and HBr respectively to 1,2-dibromo-3,4-bis(9-fluorenylidene)-cyclobut-1-ene (VIII). The cyclobutene (VIII) was prepared by the intramolecular cycloaddition of 2,3-dibromo-1,4-bis(9-fluorenylidene)buta-1,3-diene (V), which had itself been obtained by the reaction of the diacetylenediol (IV) with concd HBr in AcOH.



Scheme 2.

Any possibility that the dimer of II and X are the tail-to-tail cyclodimerization products (for example, XIV for the dimer of X) can be rejected, because the absorption bands of the dimers of II and X in the visible region are not assignable to the tail-to-tail dimers containing only a buta-1,3-diene chromophore. In order to clarify the structures of VI and XI, some addition and elimination reactions were investigated on XI.

The reaction of XI with HBr afforded the 1,4-



Scheme 3.

addition product (XV). The heating of XV in MeOH-THF afforded the methanolysis product (XVIII). On the NMR spectra, the CH_2 of both XV and XVIII appeared as two AB-type doublets, centered at 6.20 and 6.45 and at 5.88 and 6.11 τ respectively. Because these signals were little affected by raising temperature to 150 °C, the magnetic nonequivalence of the two hydrogens of CH_2 is probably due to an assymmetry effect. The CHD proton signals of XV-*d* and XVIII-*d* appeared as two singlets at 6.22 and 6.43 and at 5.92 and 6.13 τ respectively. This splitting of the CHD proton singal is also due to an assymmetry effect. These data support the structure of XI.

The reduction of XV with $NaBH_4$ afforded XVII, which showed CH, CH_2, and CH_3 signals at 4.95 (s), 7.54 (q), and 8.53 τ (t) respectively. This formation of the CH_3 group supports the presence of the *exo*-methylene moiety in XI. The multiplicity of the latter two signals suggests the presence of a long-range coupling between them.

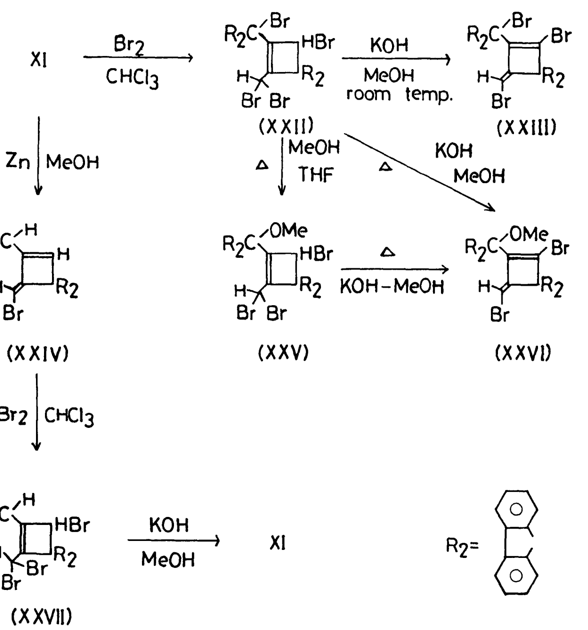
The reaction of XV and XVIII with Zn afforded XVI and XIX respectively. The NMR signals of the $=CH_2$ protons of XVI and XIX appeared at 5.83 and 5.98 and at 5.93 and 6.06 τ respectively. The absence of spin-spin coupling between the two geminal protons of $=CH_2$ is likely, because it has been established that such a coupling of the *exo*-methylene bonded to cyclobutene ring is not detectable.[3] Of the two $=CH_2$ proton signals of XVI and XIX, that at higher magnetic field can be assigned to the hydrogen directed toward the spiro-fluorene ring, therefore it is shielded by this ring.

XVIII-*d*, which was derived from XV-*d*, was allowed to react with Zn to afford a 1 : 1 mixture of XX and XXI. In the NMR spectrum of this mixture, the intensities of the signals at both 5.96 and 6.09 τ were about one half of those of the corresponding signals of XIX. These results also support the structure of XI.

The addition of Br_2 to XI afforded the 1,4-addition product (XXII). The treatment of XXII with KOH–MeOH at room temperature and at an elevated temperature under reflux afforded XXIII and XXVI respectively. The latter may be formed by the 1,4-elimination of HBr, accompanied by the methanolysis of Br on the fluorene ring, because the heating with KOH–MeOH of XXV, which had been prepared by the methanolysis of XXII, afforded XXVI (Scheme 4).

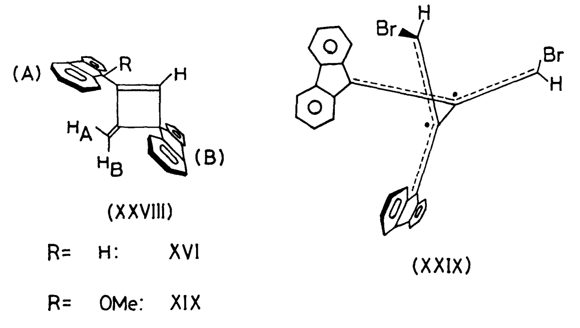
The heating of XI with Zn in MeOH afforded XXIV, which showed three proton signals at 3.28 (=CH), 5.08 (=CH), and 5.15 τ (CH), in an equal integral ratio. The addition of Br_2 to XXIV afforded XXVII in a 60% yield. The dehydrobromination of XXVII with KOH–MeOH afforded the original dimer (XI). All these reactions again support the structure of XI (Scheme 4).

The geometry around the bromomethylene moiety of XI was determined on the basis of the following data. The signal of the olefinic proton of XI appeared at such a lower field that it overlapped the signals of aromatic protons (1.90—2.86 τ), probably because of a deshielding effect by the biphenylene moiety bonded to *exo*-methylene carbon. For by the same reason, the olefinic proton of VI appeared at 2.85 τ. If the reverse geometry of XI (XIII) is correct, this olefinic proton must be shielded by the spiro-fluorene ring and resonate at a much higher magnetic field. Studies of a molecular model also suggest that the geometry of XIII is unfavorable, because of a serious steric repulsion between the 9-fluorenylidene group and the Br of the bromomethylene moiety.



Scheme 4.

However, there is still a question why the difference between the chemical shifts of the two methylene protons of XVI or XIX is so small-less than 0.15 ppm. A plausible answer to the question is that the H_A of XVI or XIX is shielded by the fluorene-ring (A) which is arranged almost perpendicular to the four-membered ring and then faces H_A, and that the shielding is comparable to that of H_B by the fluorene-ring (B) (see the XXVIII shown in Scheme 5).



Scheme 5.

It has been reported[4,5] that the thermal [2+2] cycloaddition of allene often proceeds *via* the biallyl biradical intermediate, and that the most easily formed conformation for the biradical was that in which the two flat allylic ends were orthogonal and in which the larger one of the substituents on each terminal carbon was inward; ring closure was assumed to be faster than the rotation of the parts of the allylic system to form other conformers. However, some instances which do not follow this tendency because of steric bulkiness have also been reported.[6,7]

The dimerization of X can be formulated by assuming XXIX as an intermediate (Scheme 5). So as to avoid the steric interaction between the fluorene ring and Br, the cyclization of XXIX must proceed *via* its favorable conformation, in which Br is outward, thus finally affording the dimer of the most favorable geometry around the *exo*-methylene moiety (XI).

The contrast between the unusual[8,9] head-to-tail dimerization of X to afford XI and the head-to-head dimerization of 3-chloro-1,1-diphenylpropa-1,2-diene (II) to afford 3,4-dichloro-1,2-bis(diphenylmethylene)-cyclobutane (III)[1] is probably due to a much bigger steric interaction between non-flexible fluorene rings than that between flexible diphenylmethyl groups. It has been reported that the four phenyl rings of III are arranged as a propeller, and that they are free from steric interactions among them.[4]

Experimental

All the melting points are uncorrected. The IR, UV, and NMR spectra were measured in Nujol mull, $CHCl_3$, and $CDCl_3$ respectively. The mass spectra were measured with an ionization energy of 75 eV.

Reaction of II with HCl. To an ice-cooled solution of II (6.2 g) in AcOH (60 ml), we added concd HCl (10 ml) under stirring over a period of 30 min. The stirring was continued for 1.5 hr under cooling with an ice-bath. The solid thus precipitated was filtered and washed with water and then with MeOH. The recrystallization of the dried solid from AcOEt afforded VI as orange prisms; 5.5 g (80%); mp 225 °C (lit,[1] mp 223—224 °C). NMR: 1.9—2.8 (m, Ph, 16H), 2.85 (s, =CH, 1H), and 4.24 τ (s, CH, 1H).

Isolation of X. Into an ice-cooled solution of II (4.73 g) in AcOH (60 ml), concd HBr (10 ml) was stirred over a of 30 min; the stirring was then continued for 1.5 hr under cooling with an ice-bath. The solid thus precipitated was filtered and washed repeatedly with water and then with MeOH. The solid was dissolved in ice-cooled acetone. Water was added to this solution, after which the solution was allowed to remain in a refrigerator to afford X as yellow needles; 5.15 g (86%). During the measurement of the melting point, X dimerized to XI and melted at 207.5—208.5 °C. IR: 1940 cm^{-1} (C=C=C).

Found: C, 67.15; H, 3.35%. Calcd for $C_{15}H_9Br$: C, 66.94; H, 3.37%.

Thermal Dimerization of X. A solution of X (3.8 g) in benzene (50 ml) was heated under reflux for 30 min. The crude crystals which remained after the evaporation of the solvent were recrystallized from AcOEt to afford XI as orange prisms; 3.0 g (80%); mp 207.5—208.5 °C. IR: 1150 cm^{-1}; λ_{max}: 266 (ε, 46800), 274 (51400), and 380 nm (32800); NMR: 1.9—2.8 (m, Ph and =CH, 17H) and 4.15 τ (s, CH, 1H).

Found: C, 67.25; H, 3.34%. Calcd for $C_{30}H_{18}Br_2$: C, 66.94; H, 3.37%.

Synthesis of VIII. Into an ice-cooled solution of IV (0.6 g) in AcOH (30 ml), we added concd HBr (5 ml) over a period of 30 min. The stirring was continued for 1.5 hr. The reddish-purple crystals thus formed were filtered and washed repeatedly with water and then with MeOH to afford V; 0.46 g (54%); IR: 1945 cm^{-1} (C=C=C). A solution of V (0.4 g) in benzene (10 ml) was heated under reflux for 30 min. The recrystallization from AcOEt of the crude product obtained by the evaporation of benzene afforded VIII as orange yellow needles; 0.28 g (70%); mp 221.5—222 °C. λ_{max}: 226 (ε, 53700), 275 (54900), 343 (32300), and 375 nm (31600).

Found: C, 67.46; H, 2.90%. Calcd for $C_{30}H_{16}Br_2$: C, 67.19; H, 3.01%.

Addition of Br_2 to VIII. Into a solution of VIII (0.2 g) in $CHCl_3$ (50 ml), a solution of Br_2 (0.15 g) in $CHCl_3$ (5 ml) was stirred over a period of 20 min. After the stirring had continued for 30 min, the solvent was evaporated to leave crude crystals. The recrystallization of the crystals from AcOEt afforded VII as reddish-purple prisms; 0.22 g (80%); mp 235—237 °C. λ_{max}: 278 (ε, 38600), 338 (8950), and 502 nm (23900); NMR: 1.35—3.36 τ (m, Ph).

Found: C, 51.53; H, 2.40%. Calcd for $C_{30}H_{16}Br_4$: C, 51.77; H, 2.32%.

Addition of HBr to VIII. Through a solution of VIII (0.2 g) in $CHCl_3$ (50 ml), HBr was bubbled for 10 min. The subsequent evaporation of the solvent left crude crystals. Recrystallization from AcOEt afforded IX as reddish-purple needles; 0.22 g (85%); mp 219—221 °C. λ_{max}: 270 (ε, 30500), 328 (12700), and 472 nm (21400); NMR: 1.55—3.25 (m, Ph, 16H) and 3.90 τ (s, CH, 1H).

Found: C, 58.54; H, 2.82%. Calcd for $C_{30}H_{17}Br_3$: C, 58.38; H, 2.78%.

Addition of HBr to XI. Through a solution of XI (0.93 g) in $CHCl_3$ (20 ml), HBr was bubbled for 5 min. The subsequent evaporation of the solvent left crude crystals. Recrystallization from AcOEt afforded XV as pale yellow plates; 1.0 g (94%) mp 165—167 °C. λ_{max}: 253 (ε, 90000), 280 sh (53600), 295 sh (34500), and 306 sh nm (19200); NMR: 1.9—2.9 (m, Ph, 16H), 4.79 (s, CH, 1H), 6.20 (d, J=10 Hz, CH, 1H), and 6.45 τ (d, J=10 Hz, CH, 1H).

Found: C, 57.92; H, 2.94%. Calcd for $C_{30}H_{19}Br_3$: C, 58.19; H, 3.09%.

The addition of DBr to XI by means of the same procedure as that of HBr addition afforded XV-*d* in a 90% yield. NMR: 1.9—2.9 (m, Ph, 16H), 4.79 (s, CH, 1H), 6.22 (s, CHD, 1/2H), and 6.43 τ (s, CHD, 1/2H).

Methanolysis of XV. A solution of XV (0.46 g) in MeOH–THF (1 : 1) (30 ml) was heated under reflux for 1 hr. The recrystallization from AcOEt of the crude crystals obtained by the evaporation of the solvent afforded XVIII as pale yellow plates; 0.39 g (93%); mp 173—175 °C. IR: 1085 cm^{-1} (OMe); λ_{max}: 274 (ε, 64300), 285 sh (5000), and 305 sh nm (1100); NMR: 2.0—2.8 (m, Ph, 16H), 5.13 (s, CH, 1H), 5.88(d, J=10 Hz, 1H), 6.11 (d, J=10 Hz, 1H), and 7.06 τ (s, OCH_3, 3H).

Found: C, 65.48; H, 3.73%. Calcd for $C_{31}H_{22}OBr_2$: C, 65.28; H, 3.88%.

The methanolysis of XV-*d* by means of the same procedure as was used for XV afforded XVIII-*d* in a 90% yield. NMR: 2.1—2.8 (m, Ph, 16H), 5.13 (s, CH, 1H), 5.91 (s, CHD, 1/4H), 6.12 (s, CHD, 3/4H), and 7.07 τ (s, OCH_3, 3H).

Debromination of XVIII. A mixture of XVIII (0.2 g), Zn-powder (0.7 g), and MeOH (70 ml) was heated under reflux for 1 hr. The Zn-powder was then filtered off, after which the filtrate was evaporated to dryness to leave crude crystals. Recrystallization from AcOEt then afforded XIX as pale yellow prisms; 0.99 g (68%); mp 175.5—177 °C. IR: 1665 (C=C) and 1110 and 1080 cm^{-1} (OMe); λ_{max}: 249 (ε, 27400), 268 (25600), 273 sh (24700), 297 sh (10000), and 310 nm (9300); NMR: 2.2—2.8 (m, Ph, 16H), 3.28 (s, =CH, 1H), 5.93 (s, =CH, 1H), and 6.06 τ (s, =CH, 1H); *m/e* (relative intensity): 410 (M^+, 10), 379 (M^+–OMe, 10), 215 (M^+–(9-methoxyfluorenyl), 24), 195 (9-methoxyfluorenyl, 100), and 180 (fluorenone, 22).

Found: C, 90.59; H, 5.22%. Calcd for $C_{31}H_{22}O$: C, 90.69; H, 5.40%.

The debromination of XVIII-*d* with Zn by means of the same procedure as was used for XVIII afforded a 1 : 1 mixture of XX and XXI. NMR: 2.2—2.8 (m, Ph, 16H), 3.29 (s, =CH, 1H), 5.96 (s, =CHD, 1/2H), 6.09 (s, =CHD, 1/2H), and 7.01 τ (s, OCH_3, 3H).

Debromination of XV. A mixture of XV (0.7 g), Zn-powder (2 g), and acetone (50 ml) was heated under reflux for 1.5 hr. The Zn-powder was then filtered off, after which the filtrate was evaporated to dryness to leave crude crystals. Recrystallization from AcOEt afforded XVI pale yellow prisms; 0.38 g (90%); mp 177—179 °C. IR: 1660 (C=C) and 880 cm^{-1} (=CH); λ_{max}: 252 (ε, 87700), 264 (79500), 290 (32700), 303 (29200), and 309 nm (23400); NMR: 2.1—2.9 (m, Ph, 16H), 3.41 (s, =CH, 1H), 4.99 (s, CH, 1H), 5.83 (s, $=CH_2$, 1H), and 5.98 (s, $-CH_2$, 1H); *m/e* (relative intensity): 380 (M^+, 11), 215 (M^+-fluorenyl, 100), and 165 (fluorenyl, 30).

Found: C, 94.77; H, 5.06%. Calcd for $C_{30}H_{20}O$: C, 94.70; H, 5.30%.

Reduction of XV with $NaBH_4$. A solution of XV (0.68 g) and $NaBH_4$ (0.4 g) in MeOH-THF (1 : 1) (80 ml) was allowed to remain at room temperature for 1 hr. The subsequent evaporation of the solvent left crude crystals, which were then washed with water and dried. Recrystallization from MeOH-AcOEt afforded XVII as pale yellow needles; 0.4 g (90%); mp 162—163 °C. λ_{max}: 266 sh (ε, 25900), 269 (26200), 274 sh (22700), 280 sh (19400), 296 (10000), and 304 nm (10800); NMR; 2.1—2.9 (m, Ph, 16H), 4.95 (s, CH, 1H), 7.54 (q, J=2.5 Hz, CH_2, 2H), and 8.53 τ (t, J=2.5 Hz, CH_3, 3H).

Found: C, 94.05; H, 5.50%. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80%.

Addition of Br_2 to XI. To a solution of XI (0.5 g) in $CHCl_3$ (20 ml), we added a solution of Br_2 (0.5 g) in $CHCl_3$ (5 ml) over a period of 30 min. The crude crystals which remained after the evaporation of the solvent were recrystallized from acetone to afford XXII as pale yellow prisms; 0.48 g (83%); mp 161—162 °C. λ_{max}: 253 (ε, 90000), 280 sh (53600) 295 sh (34500), and 306 sh nm (19200); NMR: 1.95—2.85 (m, Ph, 16H), 3.34 (s, $CHBr_2$, 1H), and 4.89 τ (s, CHBr, 1H).

Found: C, 51.55; H, 2.74%. Calcd for $C_{30}H_{18}Br_4$: C, 51.62; H, 2.60%.

Methanolysis of XXII. A solution of XXII (1.08 g) in MeOH-THF (1 : 1) (60 ml) was heated under reflux for 2 hr. The subsequent evaporation of the solvent left crude crystals. Recrystallization from acetone afforded XXV as pale yellow prisms; 0.84 g (90%); mp 170.5—171.5 °C. IR: 1645 (C=C) and 1100 and 1090 cm^{-1} (OMe); λ_{max}: 244 (ε, 26000), 275 (24300), and 285 nm (19900); NMR: 2.1—2.7 (m, Ph, 16H), 2.80 (s, $CHBr_2$, 1H), 5.28 (s, CHBr, 1H), and 7.07 τ (s, OCH_3, 3H).

Found: C, 57.10; H, 2.95%. Calcd for $C_{31}H_{21}OBr_3$: C, 57.35; H, 3.25%.

Dehydrobromination of XXII. A mixture of finely-powdered XXII (0.53 g), KOH (1 g), and MeOH (20 ml) was stirred at room temperature for 1 hr. The crude crystals thus formed were filtered and washed with water and MeOH. Recrystallization from AcOEt afforded XXIII as pale yellow prisms; 0.41 g (86%); mp 166.5—168 °C. λ_{max}: 253 (ε, 50300), 297 sh (13300), and 308 sh (7200); NMR: 2.15—2.85 τ (m, Ph and =CH).

Found: C, 58.50; H, 2.76%. Calcd for $C_{30}H_{17}Br_3$: C, 58.38; H, 2.78%.

Reaction of XXII with KOH-MeOH. A mixture of finely-powdered XXII (0.53 g), KOH (1.5 g) and MeOH (60 ml) was heated under reflux for 2 hr. The crude porduct formed by the addition of water to the reaction mixture was filtered, washed with water, and dried. Recrystallization from AcOEt afforded XXVI as pale yellow prisms; 0.37 g (63%); mp 179.5—181.5 °C. IR: 1070 cm^{-1} (OMe); λ_{max}: 243 (ε, 33600), 257 (33200), 271 (35800), and 309 nm (5900); NMR: 2.15—2.80 (m, Ph, 16H), 3.10 (s, =CH, 1H), and 7.15 τ (s, OCH_3, 3H).

Found: C, 65.55; H, 3.23%. Calcd for $C_{31}H_{20}OBr$: C, 65.52; H, 3.55%.

Dehydrobromination of XXV. A mixture of XXV (0.15 g), KOH (0.5 g), and MeOH (20 ml) was heated under reflux for 1 hr. The crude product formed by the addition of water to the reaction mixture was filtered, washed with water, and dried. Recrystallization from AcOEt afforded XXVI: 0.14 g (71%).

Reduction of XI with Zn. A mixture of XI (1 g), Zn-powder (2.5 g), and MeOH (100 ml), was heated under reflux for 2 hr. The Zn-powder was then filtered off, after which the evaporation of the solvent left crude crystals. Recrystallization from AcOEt afforded XXIV as colorless plates; 0.6 g (70%); mp 161—163 °C. IR: 1650 cm^{-1} (C=C); λ_{max}: 258 (ε, 75000) and 303 nm (28000); NMR: 2.2—2.9 (m, Ph, 16H), 3.28 (s, =CH, 1H), 5.08 (s, CHBr, 1H), and 5.15 τ (s, CH, 1H).

Found: C, 78.17; H, 3.91%. Calcd for $C_{30}H_{19}Br$: C, 78.44; H, 4.17%.

Addition of Br_2 to XXIV. A solution of XXIV (0.32 g) and Br_2(0.2 g) in $CHCl_3$ (10 ml) was allowed to remain at room temperature for 2 hr. The subsequent evaporation of the solvent left an oil, which was crystallized by the addition of a small amount of MeOH. Recrystallization from AcOEt afforded XXVII as colorless plates; 0.26 g (60%); mp 178—179 °C. λ_{max}: 270 (ε, 27800) and 304 nm (4600); NMR: 1.8—2.9 (m, Ph, 16H), 3.64 (s, $CHBr_2$, 1H), 4.93 (s, CHBr, 1H), and 5.23 τ (s, CH, 1H).

Found: C, 57.88; H, 2.98%. Calcd for $C_{30}H_{19}Br_3$: C, 58.16; H, 3.07%.

Dehydrobromination of XXVII. A mixture of XXVII (0.15 g), KOH (0.5 g), and MeOH (20 ml) was heated under reflux for 2 hr. The crude crystals obtained by the addition of water to the reaction mixture were recrystallized from AcOEt to afford XI; 0.12 g (92%).

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